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Intrinsic size effects in the mechanical response of taper-free nanopillars of metallic glass

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Both quantitative stress-strain curves and *in situ* transmission electron microscope observations demonstrate intrinsically strong sample size effects on the deformation mode of taper-free metallic glass pillars. With the pillar diameter gradually decreasing from 640 to 70 nm, the deformation mode evolves from (i) highly localized and catastrophic shear banding to, (ii) initially nonlocalized deformation developing toward stop-and-go shear banding accompanied by softening, (iii) apparently homogeneous and banding-less deformation but with intermittent shear events, and eventually (iv) fully homogeneous and smooth plastic flow.

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The room-temperature plastic deformation behavior of metallic glasses (MGs) is currently the focus of intense studies.[1] The plastic flow in MGs is carried by shear transformations (STs) in numerous shear transformation zones (STZs),[2–4] but the STs tend to concentrate in extremely narrow shear bands (SBs) that develop quickly to cause the failure of MG samples. The spatiotemporal evolution of STZs toward severely localized SBs remains mysterious so far. Understanding the effects of MG sample size in the micrometer to nanometer regime on mechanical response can provide insight into this fundamental issue and guide the practical design of incorporating small-volume MG into microelectromechanical devices.[5]

A number of theoretical[6,7] and experimental[8–14] studies have demonstrated that for sample dimensions at the micrometer scale shear banding is still the dominant deformation mechanism.[9–11] What happens at even smaller sample sizes (diameter D on submicrometer to nanometer scale) remains controversial. There have been debates as to whether the "homogeneous" plastic flow reported[11–14] is an intrinsic size effect or an artifact. There are two major challenging issues in this D regime. First, fabricating specimens free of geometrical imperfections and surface contaminations becomes very difficult. For example, tapering is the norm for such small pillars prepared via milling employing the focused ion beam (FIB) technique. Tapering invariably induces complicated stress states and deformation localization at the pillar-punch contact. Indeed, intentionally induced tapering was confirmed to remarkably change the apparent plasticity of bulk specimens.[15] At small sample sizes, the tapering becomes especially serious, and its effect is amplified as a constant taper gives much higher stress gradient for smaller D. Surface modifications by ion beam and redeposition are also an issue and may contribute to the unexpected hardening of nanosized MGs.[13]

Second, while a number of reports contrast different behaviors for pillars of different sizes, there have been no quantitative nanomechanical tests that systematically demonstrate exactly what the transition is like, e.g., gradual or abrupt, and if there are intermediate stages in between where the detailed evolution of the microscopic processes may shed light on the mysterious process of STs evolving toward shear banding.

In the following we demonstrate the fabrication and behavior of taper-free MG nanopillars. We will also use quantitative *in situ* compression tests inside a transmission electron microscope (TEM) to illustrate not only the morphological differences for samples of various D, but more importantly the striking difference in their stress-strain curves.

The pillars were milled by FIBs from a bulk Cu-Zr-based MG, $Cu_{47}Ti_{33}Zr_{11}Ni_6Sn_2Si_1$.[11] In the final step of milling the surfaces were polished by orienting the ion beam perpendicular to the pillars in an approximately parallel milling procedure to remove tapering and surface redeposition. Taper-free MG pillars with D ranging from 640 to 70 nm were successfully fabricated. The length-to-diameter ratio $c = L/D$ was designed at ~3.0. *In situ* compression was performed in a JEOL 2010F TEM using a recently developed Hysitron picoindenter, which is capable of high-resolution measurements of load and displacement (~0.3 μN and ~1 nm, respectively) with rapid instrument response and da ta acquisition rates.[11] Tests were performed under displacement control at a nominal strain rate of $\sim 10^{-2}$/s.

As expected, our pillars with relatively large D show severely localized shear banding, the same response as also observed for previous tapered pillars.[8–11] As an example, the behavior of a pillar with $D = 640$ nm is shown in Fig. 1(a). Immediately after an initial small local shear that accommodates the imperfect tip-punch contact, two fast-running major SBs 45° to the loading axis were triggered [Fig. 1(a)]. They cross each other and produce a major displacement burst [see the stress-strain curve in Fig. 1(b)].

Our taper-free specimens with smaller D, e.g., the $D =$ 365 nm pillar in Fig. 1(c), still show SBs but only at a later stage of compression. A SB traversing the pillar in Fig. 1(c) appears only after 8% strain, and the sample no longer fails immediately, but survives a 15% total strain [see Fig. 1(d)]. More interestingly, the initial stress response shows "apparent hardening" in the engineering stress-strain curve, which is immediately taken over by softening with the onset of the SB. The initial apparent hardening is due to a global increase of the effective load-bearing area throughout the gauge section along with continued compression, and the true stress shows almost no real hardening (see the inset). The "apparently hardenable" deformation however, is not uniform, with jerky-type stress drops observable. These events are less pronounced than those in the later SB process, and no transient shear processes corresponding to the jerky events are observed in the structure

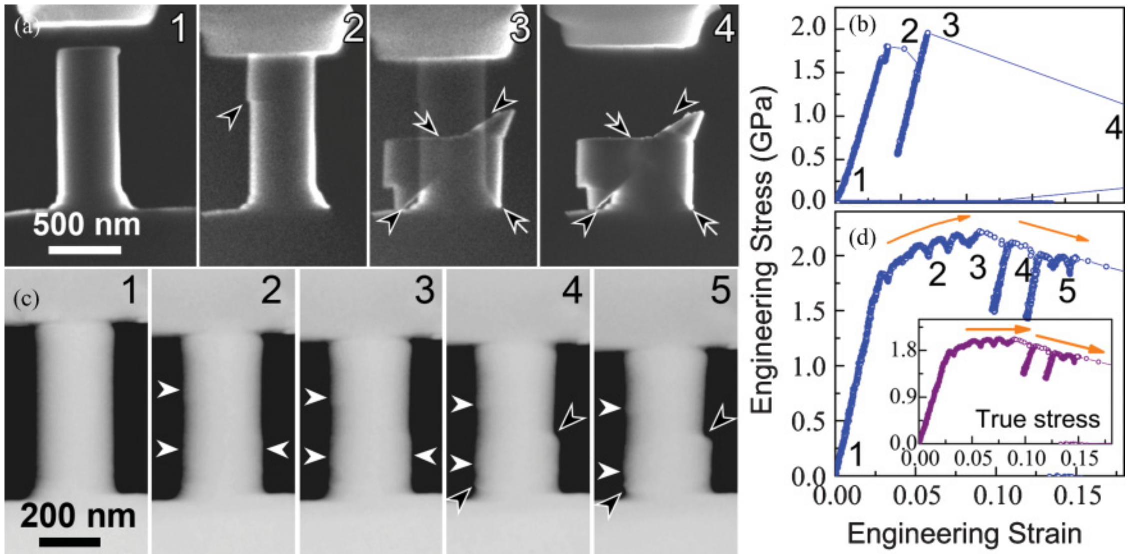

FIG. 1. (Color online) Dark-field TEM images (still frames from video) showing the deformation of (a) 640 nm and (c) 365 nm diameter pillars: the numbering in (a) and (c) corresponds to the instances numbered in the stress-response curves in (b) and (d), respectively, the inset in (d) being true stress. Open and solid white arrows annotate SBs and local bumps, respectively.

evolution; instead, irregular local surface bumps are gradually developed within the well-defined gauge section. Importantly, the initial "hardening" in engineering stress is an intrinsic behavior fundamentally different from the previously observed load increase in the compression of tapered pillars; there the apparent hardening is due to a diameter change associated with the pressing of a tapered "tip." The range of deformation before the onset of shear banding eluded previous observation because the tapered pillars can promote early formation of local SBs at the top of the pillar due to the stress gradient.[11]

The subsequent softening is due to the development of a SB initiated near a local bump formed in the prior apparent hardening stage. Noticeably, the SB is often arrested first and restarts upon further loading, producing stress serrations in the stress curve [Fig. 1(d)]. Also note that the serrations associated with the stick-slip (arrest and restart, or stop and go) of the single SB 45° to the loading axis, differs significantly from serrations observed in bulk specimens, which are often due to the onset and interaction of more and more SBs.

Upon further decreasing the sample size, SB formation becomes less and less obvious. The $D = 125$ nm exhibits apparently homogeneous deformation (Fig. 2 and Ref. 16). The term "homogeneous deformation" here[8,10] refers to plastic deformation that is distributed all over the sample and is approximately axisymmetric, in contrast with the severely localized SB features normally expected for MGs at room temperature. As seen in Fig. 2(a), initially bulging/swelling occurs at the top of the pillar. With increasing displacement the bulge does not extend downward; instead, plastic flow starts in another area some distance ahead, where the side surfaces continuously bow out, leaving two seemingly "necked" regions on each side. Such barreling is often a sign of good plasticity. In the stress-strain curve [Fig. 2(c)], one observes an apparently monotonic hardening, again due to the enlarged cross-sectional area along with compression.

Remarkably, although the pillar shows a morphologically homogeneous deformation, it does not at the same time show a smooth stress response. There are still noticeable intermittent stress drops in Fig. 2(c) indicative of transient shear events within the pillar. It means that the morphologically homogeneous plasticity is "intrinsically" inhomogeneous, and is a collective behavior of many transient, local flow events. These mild shear events are small and not catastrophic. They do not organize into morphologically noticeable shear bands, and would not have been detected without quantitative tests and a sufficiently fast machine response made possible by the picoindenter.

Interestingly, the size of the serrations is not uniform. For example, there is a relatively larger stress drop between frames 2 and 3 in Fig. 2. It is presumably associated with a larger local shear event's interior of the specimen. However, this shear event is still small, and does not develop into a harmful SB. This is confirmed by the fact that the stress quickly recovers to its predrop level, and the homogeneous barreling is continuously developed, subsequently accommodating large plastic strain. The serrations and the scatter in magnitude of it, in fact, is a useful measurement of "inhomogeneity." It is more pronounced in Fig. 1 for thicker pillars and diminishes for smaller pillars, as will be further demonstrated.

A three-dimensional (3D) finite element modeling (FEM) study is employed to analyze the local stress state in association with the deformation behaviors.

As shown in Fig. 2(b), the deformation of the MG nanopillar can be satisfactorily predicted by the FEM that treats the material as an isotropic elastic-plastic body with homogeneous plastic flow. Frames 1–3 in Fig. 2 show the evolution of the plastic strain and the gradually developing shape of the specimen; here the bulging at the tip and barreling far ahead are consistent with the experimental observations. The tip bulging can be interpreted as a result of high local shear stress, as shown

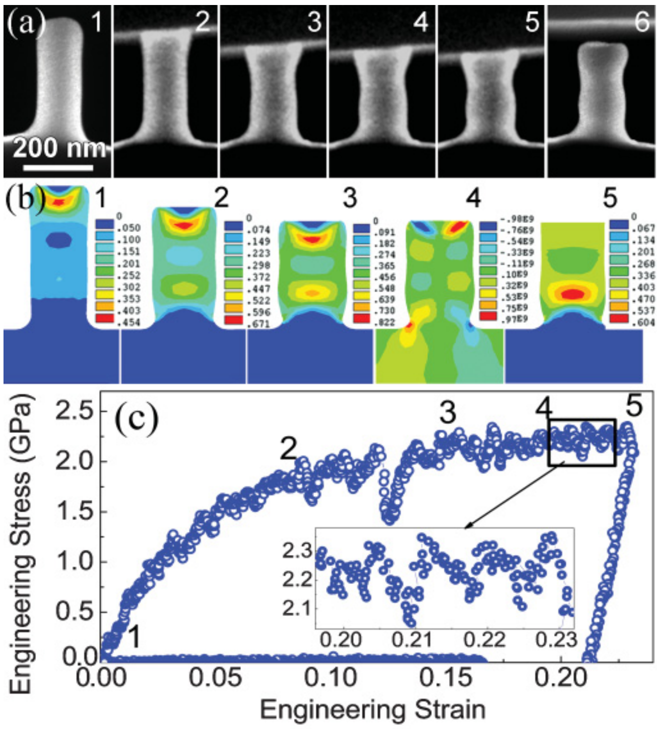

FIG. 2. (Color online) Shear-band-less deformation of a 125 nm diameter pillar: (a) video frames grabbed at points 1–6 in the stress-strain plot in (c); (b) 3D FEM of the compression by treating the MG as an isotopic, elastic ideal–plastic solid with frames 1–3 showing the evolution of Mises strain and the deformed shape of a pillar with a rounded tip, taking into account tip-punch friction, frame 4 being shear stress at the same displacement as in frame 3, and frame 5 showing compression of a modeled pillar with flat top surface and zero friction.

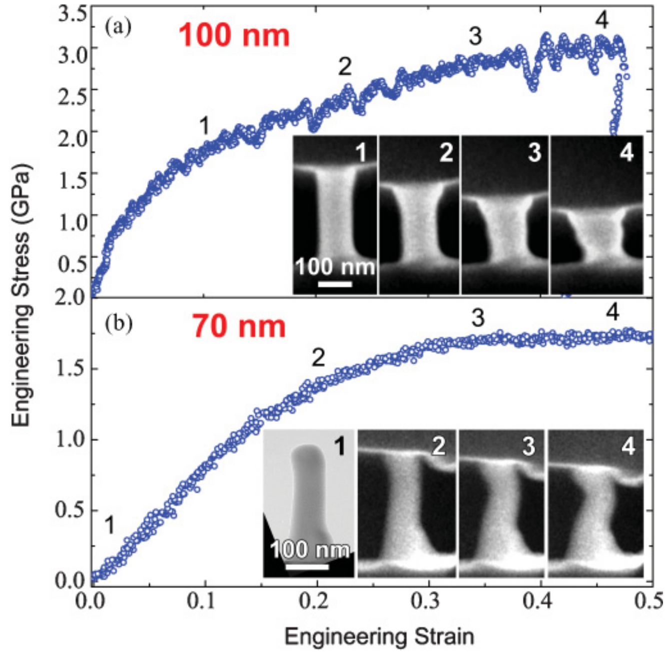

FIG. 3. (Color online) Stress and morphological evolutions of nanopillars with diameters of (a) 100 nm and (b) 70 nm, respectively, as functions of strain.

in frame 4 of Fig. 2(b), due to the pillar-punch friction and/or some roundness of the pillar top. This is confirmed by the fact that a simulated specimen with a flat top and zero pillar-punch friction [frame 5 in Fig. 2(b)] does not show a bulging at the tip. The continuous barreling in the middle is more likely due to the constraint at the base and the shear stress concentration there, since it is always observed independent of the roundness of the tip and/or the tip-punch friction. Barreling was also occasionally observed previously in the compression of some bulk MG-based composites; there the relatively large plasticity was, however, mediated by well-developed, profuse SBs in the presence of nanocrystallites embedded in the MG matrix.[17] In addition, the "shear-banding-less" barreling occurring in the middle section of the pillar rules out the possibility that it is an effect of pillar-punch friction as in tapered pillars where deformation always occurs preferentially at the tip-punch contact. This barreling has never been observed before on tapered pillars, and is believed to be a norm of homogeneous deformation for the pillar-shaped samples that are made taper-free.

Experiments on the taper-free pillars with further decreasing pillar size are getting more challenging, as they are becoming more and more sensitive to any misalignment and geometric imperfections in the pillars. However, important information is still obtained through the testing of $D = 100$ nm and $D = 70$ nm pillars, as shown in Figs. 3(a) and 3(b), respectively. The general observation is that with smaller diameters, the pillars persist to banding-less deformation and the serrations are getting less noticeable, as well as more uniform. In Fig. 3(a), the $D = 100$ nm pillar shows gradually developed misalignment, especially at the later stage (>20% plastic strain), and thus a less noticeable barreling effect compared to that in Fig. 2.

Figure 3(b) shows the test on the $D = 70$ nm pillar. Note that the size here reaches the experimental limit for fabricating geometrically "perfect" taper-free pillars through the FIB procedure. An initial slight bending shape is produced on the pillar, which during the test resulted in a noticeable bending component along with the compression. Importantly, the specimen does not show any SBs, and in addition, shows a fully smooth stress-strain curve without detectable serrations. It indicates an ultimate transition from the shear banding to homogeneous flow. However, it should be pointed out that the particular size at which a fully homogeneous deformation occurs ($D = 70$ nm here) could be influenced by the bending component.

In fact, we have recently demonstrated[11] through bending experiments, a clear size effect in small MG pillars. We have discussed through a micromechanical model that homogeneous deformation could appear earlier under bending than under compression.

Compared with tapered pillars, the present quantitative and *in situ* TEM tests on taper-free nanopillars are more informative of the intrinsic size effect. The obvious trend from highly intermittent stress-strain response toward smoother and smoother flow curves with decreasing D is a strong telling sign, in addition to the morphological observation of diminishing shear offsets, of the gradually subsiding plastic instability (localization). We captured a complete range of the progressive transition in deformation mode through four stages: (i) highly localized shear banding from the beginning; (ii) initial nonlocalized deformation gradually developing toward shear banding; (iii) banding-less but still intermittent, spatially and temporally discrete shear events; and (iv) fully homogeneous flow with smooth stress-strain response. This full spectrum is made in the absence of pillar tapering. It is unlikely to be an effect of surface modification, as the sample surfaces are clean. Ion-beam damage due to FIB cutting is also believed to be small for amorphous alloys.[9–13]

It is also not due to an effect of electron-beam irradiation recently reported for amorphous silica spheres and nanowires.[18] In fact our recent *in situ* TEM compression of slightly tapered pillars subject to similar irradiation conditions as in this study showed that those tapered pillars showed obvious shear banding even when the pillar diameter was decreased to 100 nm scale,[11] indicating that tapering rather than the e-beam plays a key role.

We reiterate that homogeneous deformation here means distributed shear transformations throughout the sample, rather than STs activated repeatedly and predominantly in the narrow SB. Even though individual STs and their groups may be discrete, they do not always localize into SBs. According to Shi and Falk[19] the degree of localization can be evaluated by a deformation participation ratio (DPR), which is the fraction of atoms that undergo a strain larger than the nominal strain of the entire sample. A fully homogeneous deformation means a DPR close to 0.5, while a highly localized deformation has a DPR near zero. In this context, our microstructure observation (SB on a specific plane versus spread-out deformation) and stress-strain responses (bursts and serrations versus smooth curves) suggest that by decreasing D from micrometer to nanometer scale, the DPR should increase from $\sim$0 to $\sim$0.5.

The possible causes for the sample size dependence of the dominant deformation mode have been discussed by several authors.[8–13] Volkert *et al.*[10] and others[8,13] have argued that when the elastically stored energy in the small pillar volume is not sufficient to compensate for the energy required to expand the area of a SB traversing the pillar, homogeneous deformation would take over. We further discussed that when a SB cannot be self-sustaining upon elastic unloading, the initiated SB can stop first and then go upon further loading.[11] The current observation further indicates that locally organized shear events, each involving many STZs but not evolving into SBs, can still emerge. That is why we observe intermediate stages in between severe localization and homogeneous flow.

In general, the sample size effect can be understood in the following simple terms. MGs can plastically deform through the STs, provided there is no SB that prematurely fails the sample. The milder the first SBs, the more chance for other later SBs, as well as the STs outside the SBs, to contribute to the overall sample strain, and the deformation would appear more homogeneous. Apparently, with decreasing D the incipient shear band becomes slower in its shear speed, its shear offset is smaller, and the temperature inside the band is lower,[20] giving STs elsewhere opportunities to come into play. Indeed, we observed that with decreasing D, the serrations become less noticeable and more uniform in the stress-strain curves. At small enough sample sizes, morphologically homogeneous deformation emerges, though still accommodated by intrinsically inhomogeneous local events which have no chance to develop into a global SB. With further decreasing size, any shear localization fades off, with STs all over the sample getting to participate in the deformation, rendering fully homogeneous deformation and large sustainable plastic strains in the sample.

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[16]See supplemental material at [http://link.aps.org/supplemental/10.1103/PhysRevB.83.180201] for movie recorded *in situ* in a TEM during compression of the 125 nm diameter MG pillar. The speed of the clip is 300% of the rate at which it was recorded.

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